

PATENT SPECIFICATION

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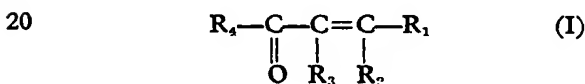


(54) PROCESS FOR THE PRODUCTION OF α,β -UNSATURATED KETONES

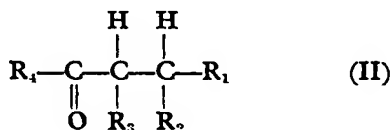
(71) We, VEB LEUNA-WERKE
 "WALTER ULBRICHT", of DDR-422
 Leuna 3, Eastern Germany, a Corporation
 organised and existing under the laws of
 5 Eastern Germany, do hereby declare the
 invention, for which we pray that a Patent
 may be granted to us, and the method by
 which it is to be performed, to be particularly
 described in and by the following state-
 10 ment:—

This invention relates to the production of
 α,β - unsaturated ketones, and is an improve-
 ment of the process described and claimed in
 our co-pending Application No. 3489/71
 15 (Serial No. 1340611).

The Application referred to above describes
 and claims a process for the production of
 α,β - unsaturated ketones of the general
 formula I:



in which formula R_1 and R_4 are the same or
 different, R_1 , R_2 and R_3 being chosen from
 hydrogen and optionally substituted alkyl,
 cycloalkyl, aryl or heterocyclic groups, and R_4
 25 being an optionally substituted alkyl, cyclo-
 alkyl, aralkyl, aryl or heterocyclic group, or in
 which two or more of the said groups with
 appropriate valency modification form one or
 more closed rings, from ketones of the general
 30 formula II,



in which formula R_1 and R_4 are as defined

above. The process is characterised by reaction
 of ketones of the general formula II with a
 compound of a platinum group metal in a
 35 bivalent or a higher valency state, at a tem-
 perature of between -15 and 180°C , prefer-
 ably between 20 and 120°C . The platinum
 group metal is defined as one chosen from
 ruthenium, rhodium, palladium, osmium,
 40 iridium and platinum.

The reaction of the ketones of the general
 formula (II) with the platinum group metal
 compounds normally takes place in a stoichio-
 metric quantity.
 45

It has been found, in accordance with this
 invention, that the consumption of the said
 platinum group metal compounds can be con-
 siderably reduced if, in place of stoichio-
 metric quantities, catalytic quantities of the
 compounds of the platinum metal are used in
 the presence of peroxy compounds, and if the
 reaction is effected at a temperature between
 30 and 160°C , preferably between 60 and
 110°C. The catalytic quantities are from
 1/100 and 1/1000 mol of the platinum group
 metal compound per mol of ketone reactant.
 Among the suitable ketones for this single-
 stage process are for instance methyl isobutyl
 ketone, di - n - propyl ketone, methyl - n -
 60 amyl ketone, cyclopentanone, 2 - methylcyclo-
 pentanone, 3 - methylcyclopentanone, cyclo-
 hexanone, 2 - methylcyclohexanone, 3 -
 methylcyclohexanone, 4 - methylcyclo-
 hexanone, 4 - *tert.* - butylcyclohexanone,
 65 3,3,5 - trimethylcyclohexanone, cycloheptanone
 and cyclododecanone. The highest yields are
 obtained with cyclohexanone and cyclo-
 pentanone.

The reactant ketones can be used in sub-
 stance or diluted with a solvent, preferably
 70 *tert.* - butanol.

A particularly suitable peroxy compound is
tert. - butyl hydrogen peroxide. Other peroxy

compounds can nevertheless be employed, such as for example hydrogen peroxide or 2 - methylbutyl - 2 - hydroperoxide.

Among the suitable catalysts are for instance 5 palladium(II) - chloride, rhodium(III) - chloride and hexachloroplatinic(IV) - acid.

The reaction is preferably carried out in a stirring vessel, and at normal or increased pressure according to the boiling point of the 10 initial reactant.

The reaction products are preferably worked up by separating an organic phase of the reaction products from the accompanying material by steam distillation or vacuum distillation, the said phase being further sub- 15 jected to fractionation or distillation to obtain the required ketone.

The residue of the steam distillation or of the vacuum distillation contains the catalyst, 20 which is to some extent present in metallic form and which can be re-used after regeneration.

The new synthesis enables the α,β - unsaturated ketones to be obtained generally 25 with a maximum yield of 80%.

In the following examples the yield percentages given are based on the quantity of peroxy compound converted.

Example 1

30 2.0 g of PdCl_2 were dissolved in 2 ml of concentrated hydrochloric acid solution by heating, and after the hydrochloric acid had been removed by evaporation to produce a residue having a viscous consistency, 245 g of cyclohexanone was added. The resulting 35 solution was heated to 90°C and, at this temperature, was added 112 g of *tert.* - butyl hydroperoxide dropwise. The reaction mixture was then heated for 4 hours at 90°C; 40 the organic products were separated from the catalyst by steam distillation. The organic phase was dried by means of sodium sulphate and worked up by fractional distillation.

45 This process produced, at 59°C and 12 mm Hg, 74 g of cyclohexenone - (3), equivalent to a yield of 70%.

Example 2

50 In a similar way to Example 1, 2.0 g of PdCl_2 was dissolved in concentrated hydrochloric acid, to which solution was added 210 g of cyclopentanone. The resulting solution was heated to 85°C, and at this temperature 112 g of *tert.* - butyl hydroperoxide was added dropwise. The reaction mixture was then 55 heated to 85°C for a further 4 hours. The reaction products were separated by vacuum distillation from the catalyst at 12 mm Hg, and then distilled by fractionation.

60 At 40°C and 12 mm Hg, this process produced 38 g of cyclopentenone, equivalent to a yield of 75%.

Example 3

In a similar way to Example 1, 2.0 g of PdCl_2 were dissolved in concentrated hydrochloric acid, and to this solution was added 65 224 g of 3 - methylcyclohexanone. The resulting solution was heated to 90°C and at this temperature 90 g of *tert.* - butyl hydroperoxide was added dropwise. The reaction mixture was then heated to 90°C for a further 70 4 hours. The organic products were separated from the catalyst by steam distillation, and the organic phase was fractionally distilled after having been dried by means of sodium sulphate. 75

At 81—83°C and 22 mm Hg, 19 g of 5 - methylcyclohexenone - (3), corresponding to a yield of 16%, was obtained, and at 94—96°C and 22 mm Hg, 38 g of 1 - methyl- 80 cyclohexenone - (3), corresponding to a yield of 48%, was obtained.

Example 4

In a similar way to Example 1, 2.0 g of PdCl_2 were dissolved in concentrated hydrochloric acid and to this solution was added 85 227 g of di - *n* - propylketone. The resulting solution was heated to 90°C and, at this temperature, 90 g of *tert.* - butylhydroperoxide was added dropwise. The reaction mixture was then heated to 90°C for a further 4 hours, 90 and the organic products were separated from the catalyst by distillation with steam. The organic phase was dried by means of sodium sulphate and fractionally distilled.

At 74—75°C and 12 mm Hg, 26 g of 95 *trans* - heptene - (2) - one - (4) was obtained, equivalent to a yield of 64%.

Example 5

In a similar way to Example 1, 2.0 g of PdCl_2 were dissolved in concentrated hydrochloric acid, to which solution was added 100 228 g of methyl - *n* - amylketone. The resulting solution was heated to 70°C, and at this temperature 90 g of *tert.* - butyl hydroperoxide was added dropwise. The reaction mixture was then kept at this temperature for a 105 further 6 hours and the organic products were separated from the catalyst by distillation with steam. The organic phase was fractionally distilled after having been dried with 110 sodium sulphate.

At 62°C and 15 mm Hg, 25 g of *trans* - heptene - (3) - one - (2) was produced, equivalent to a yield of 51%.

Example 6

115 A solution of 2.0 g of RhCl_3 in 245 g of cyclohexanone was heated to 90°C while stirring, and to this was added 112 g of *tert.* - butyl hydroperoxide in drops. The solution was kept at 90°C for 6 hours. The organic 120 products were separated from the catalyst by distillation with steam and the organic phase

was distilled by fractionation after having been dried with sodium sulphate.

At 59°C and 12 mm Hg, 48 g of cyclohexenone - (3) was produced, equivalent to a yield of 69%.

Example 7

To a solution of 4.5 g of hexachloroplatinic(IV) acid in 245 g of cyclohexanone was added dropwise, whilst stirring and at 90°C, 120 g of 2-methylbutyl - (2) - hydroperoxide. The solution was kept at this temperature for 6 hours. The reaction products were separated from the catalyst by distillation with steam, and the organic phase was distilled by fractionation after having been dried with sodium sulphate.

At 58—59°C and 12 mm Hg, 45 g of cyclohexenone - (3) was produced, equivalent to a yield of 52%.

Example 8

In a similar way to Example 1, 2.0 g of PdCl_2 was dissolved in concentrated hydrochloric acid and added to 150 g of cyclohexanone and 500 g of an 8%-strength solution of hydrogen peroxide in *tert.* - butanol. The mixture was heated for 30 minutes under reflux, and the organic products were then separated from the catalyst by distillation with steam. The organic phase was distilled by fractionation after having been dried with sodium sulphate.

At 58—59°C and 12 mm Hg, 37 g of cyclohexenone - (3) was produced, corresponding to a yield of 71%.

Example 9

In a similar way to Example 1, 2.0 g of PdCl_2 was dissolved in concentrated hydrochloric acid and added to 100 g of *n* - butyrophenone. The resulting solution was heated to 90°C and, at this temperature, 70 g of *tert.* - butyl hydroperoxide was added dropwise. The reaction mixture was then heated for 5 hours to 90°C and the organic products were separated from the catalyst by distillation with steam. The organic phase was dried via sodium sulphate and worked up by fractional distillation.

At 122—124°C and 12 mm Hg, 20 g of phenyl propenyl ketone was produced, equivalent to a yield of 55%.

WHAT WE CLAIM IS:—

1. A process for the production of α,β - unsaturated ketones of the general formula I as hereinbefore defined, from ketones of the general formula II as hereinbefore defined, which process consists in reacting a compound of the general formula II with from 1/100 to 1/1000 mol of a compound of a platinum group metal in a bivalent or higher valency state per mol of reactant ketone in the presence of a peroxy compound at a temperature between 30 and 160°C.

2. Process in accordance with Claim 1, wherein the temperature is between 60 and 110°C.

3. Process in accordance with Claim 1 or Claim 2, wherein the reactant ketone is used in a solvent.

4. Process in accordance with Claim 3, wherein the solvent is *tert.* - butanol.

5. Process in accordance with any preceding Claim, wherein the peroxy compound is *tert.* - butyl hydroperoxide.

6. Process in accordance with any preceding Claim, wherein an organic phase of the reaction products is separated from accompanying material by steam or vacuum distillation, said phase being further subjected to fractionation or distillation to obtain the required ketone.

7. Process for the production of α,β - unsaturated ketones according to claim 1 carried out substantially as herein described and exemplified.

8. α,β - unsaturated ketones when produced by the process of any preceding Claim.

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